university of groningen

University Medical Center Groningen

University of Groningen

Organic non-volatile memories from ferroelectric phase-separated blends

Asadi, Kamal; De Leeuw, Dago M.; De Boer, Bert; Blom, Paul W. M.

Published in:
Nature Materials

DOI:
10.1038/nmat2207

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Asadi, K., De Leeuw, D. M., De Boer, B., & Blom, P. W. M. (2008). Organic non-volatile memories from ferroelectric phase-separated blends. *Nature Materials*, *7*(7), 547-550. https://doi.org/10.1038/nmat2207

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 05-05-2023

Organic non-volatile memories from ferroelectric phase-separated blends

KAMAL ASADI[1], DAGO M. DE LEEUW[1,2], BERT DE BOER[1] AND PAUL W. M. BLOM[1]*

[1]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747 AG, Groningen, The Netherlands

[2]Philips Research Laboratories, High Tech Campus 4, NL-5656 AE, Eindhoven, The Netherlands

*e-mail: p.w.m.blom@rug.nl

Published online: 15 June 2008; doi:10.1038/nmat2207

New non-volatile memories are being investigated to keep up with the organic-electronics road map[1]. Ferroelectric polarization is an attractive physical property as the mechanism for non-volatile switching, because the two polarizations can be used as two binary levels[2]. However, in ferroelectric capacitors the read-out of the polarization charge is destructive[3]. The functionality of the targeted memory should be based on resistive switching. In inorganic ferroelectrics conductivity and ferroelectricity cannot be tuned independently. The challenge is to develop a storage medium in which the favourable properties of ferroelectrics such as bistability and non-volatility can be combined with the beneficial properties provided by semiconductors such as conductivity and rectification. Here we present an integrated solution by blending semiconducting and ferroelectric polymers into phase-separated networks. The polarization field of the ferroelectric modulates the injection barrier at the semiconductor–metal contact. The combination of ferroelectric bistability with (semi)conductivity and rectification allows for solution-processed non-volatile memory arrays with a simple cross-bar architecture that can be read out non-destructively. The concept of an electrically tunable injection barrier as presented here is general and can be applied to other electronic devices such as light-emitting diodes with an integrated on/off switch.

Ferroelectric materials have been extensively studied as an active medium for non-volatile data storage. Reversible spontaneous polarization is maintained even in the absence of an electric field. In a digital non-volatile memory the ferroelectric polarization can be used as two binary levels[2]. However, in ferroelectric capacitors, the read-out of the polarization charge via the detection of the current transient is carried out by applying a voltage pulse that exceeds the coercive field and, therefore, is destructive[3]. Consequently, the capacitors need to be reprogrammed after each read-out.

Non-destructive read-out requires resistive switching. Inorganic ferroelectrics are wide-band-gap semiconductors that conduct electricity owing to the presence of lattice defects such as vacancies[4]. Bistable conduction has been demonstrated in a ferroelectric Schottky diode[5]. Here, the depletion width of the diode depends on the polarization state. For a polarization parallel to the built-in field the depletion width is so small that charge carriers tunnel through the depletion zone. Consequently, the resistance of the diode is low. For a polarization antiparallel to the built-in field, the depletion width is large and the resistance is high. The binary resistance states can be read out at low bias.

Attempts to optimize ferroelectric Schottky diodes for non-volatile memory applications were not successful. The major bottleneck was that ferroelectricity and electrical conductivity are mutually exclusive in a single inorganic compound. Enhancement of the conductivity by doping strongly reduces the ferroelectric polarization because the additional free charge carriers neutralize the polarization charges. Such diodes cannot be polarized when doped, or read out when undoped. The challenge is to develop a storage medium that enables independent tuning of resistance and polarization. To merge these incompatible, orthogonal electronic properties, we used mixtures of solution-processable semiconducting and ferroelectric polymers. Blends of polymers have been advantageously used in for instance organic solar cells[6,7], electrochemical light-emitting diodes[8] and ambipolar field-effect transistors[9]. In these devices one physical property, namely the charge-carrier transport, is optimized by blending electron- and hole-transporting polymers. Here, we integrate the incompatible functionalities of ferroelectricity and conductivity. We demonstrate that the polarization field of the ferroelectric phase can be used to locally modulate the injection barrier at the semiconductor–metal contact.

Chemical structures of the polymers used are shown in Fig. 1a. Semiconducting regio-random poly(3-hexylthiophene) (P3HT) is a conjugated and rigid macromolecule, whereas the electrically insulating ferroelectric poly(vinylidenefluoride-co-trifluorethylene) (P(VDF–TrFE)) is a linear macromolecule with a large structural flexibility. Spin-cast mixtures of these two polymers from a common solvent yield a phase-separated, interpenetrating network that is both ferroelectric and semiconducting. Experimental details are presented in the Methods section. The diode geometry is shown in Fig. 1b and the operation mechanism of the diode is elucidated in Fig. 1c,d. The diode consists of a phase-separated, continuous network sandwiched between two electrodes. The current can only flow through the P3HT phase. To inject the charges an ohmic contact is required, of which the Fermi level aligns with the valence or conduction band. When the Fermi level is not aligned, the injection of charge carriers is limited, and, therefore, the current in the device is low. We deliberately use a contact, typically silver, that poorly injects into the unintentionally doped P3HT. The injection barrier, that is the difference between the silver work function (4.3 eV), as measured with a Kelvin probe, and P3HT ionization potential[10] (4.9–5.0 eV), is of the order of 0.6–0.7 eV. Figure 1c shows the band diagram at the silver contact for a pristine, unpoled diode, taken along the cross section A–B in the expanded picture of Fig. 1b.

© 2008 Macmillan Publishers Limited. All rights reserved.

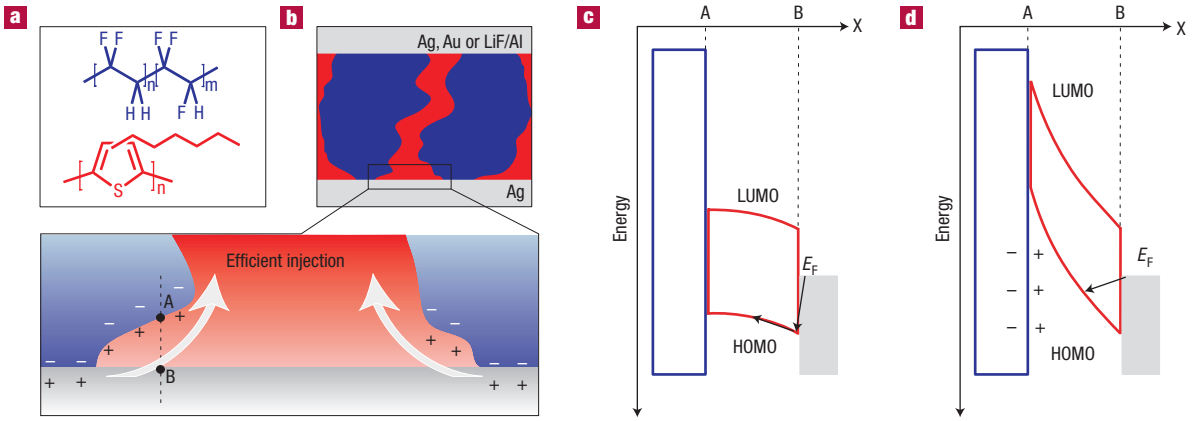

Figure 1 Schematic presentation of the operating mechanism of a polymeric ferroelectric interpenetrating network. a, Chemical structures of the semiconductor P3HT (bottom) and the ferroelectric polymer P(VDF–TrFE) (top). **b**, Schematic cross-section of a diode based on a network of semiconducting and ferroelectric polymers. **c**, Band diagram at the bottom silver contact of an unpoled diode along the cross section A–B. **d**, Band diagram at the bottom silver contact of a poled diode along the cross section A–B. Poling of the ferroelectric material yields opposite charges at the ferroelectric–semiconductor interface, induces band bending in the semiconductor and leads to enhanced charge injection.

The large injection barrier prevents efficient charge injection and the device current is low. Subsequently, the ferroelectric is poled with a negative bias at the top electrode. A schematic picture of the poled interface is shown in Fig. 1b. Owing to the poling, a negative polarization charge is built up in the ferroelectric. To neutralize the polarization charges, holes will accumulate in the semiconducting P3HT phase and/or in the silver metal electrode. The band diagram at the silver electrode along the cross section A–B is presented in Fig. 1d. The accumulated charge gives rise to strong band bending in the P3HT semiconductor. For a sufficiently thin P3HT phase this band bending effectively reduces the injection barrier at the interface between the metal and the semiconductor. The charge injection as indicated by the arrows in Fig. 1d is then strongly enhanced and the contact becomes ohmic. Similarly, poling in the opposite direction can even increase the injection barrier. The switching can be measured in an actual device when the vertical phase separation of the two polymers at the interface with the metal occurs on a length scale comparable to the accumulation width of the semiconductor, which typically amounts to 10–20 nm.

Fabrication of an interpenetrating network is achieved by using tetrahydrofuran (THF) as a common solvent for both P(VDF–TrFE) and regio random P3HT (see the Methods section for details). This semiconductor does not macroscopically crystallize during the processing, but forms an interpenetrating network. The concept, however, is general, and comparable junctions were made with other semiconductors as well. Silver is used as a poorly injecting bottom electrode. Onto the silver electrode thin films of about 140–250 nm were spin coated from THF solutions. The content of P3HT was varied between 0 and 10 wt%. As an ohmic top electrode gold was used and as a blocking contact LiF/Al was applied. Finally, the stacks were annealed at 140 °C to enhance the crystallinity of the ferroelectric β-phase of P(VDF–TrFE)[11]. Variation of the process parameters, such as drying rate, spinning speed and film thickness, hardly changed the electrical characteristics, demonstrating a large process window. The electrical transport scaled with the device area, which was varied from $0.3 \times 0.3\,mm^2$ to $4 \times 4\,mm^2$. Measurements with atomic force microscopy showed the formation of a fully phase-separated network with a lateral phase separation on a length scale of typically 200 nm. The correlation between the optical contrast and topography measured with a scanning near-field optical microscope strongly indicates that the phases are continuous (see the Supplementary Information).

Pure P(VDF–TrFE) is an electrical insulator, whereas the P3HT:P(VDF–TrFE) networks are conducting. Typical current densities (J) versus voltage (V) for a pristine, unpoled 5 wt% P3HT network with either two silver or two gold electrodes are presented in Fig. 2a. The J–V characteristics are almost linear and symmetric. The difference in current density of about one order of magnitude is due to the different injecting properties of the electrodes. On P3HT gold is an almost ohmic contact whereas silver is a poorly injecting contact with an estimated injection barrier of about 0.7 eV. A comparable reduction in current density has been reported for the injection-limited electron current in methanofullerene diodes[12], where a change in injection barrier of 0.76 eV resulted in a change in current density by two orders of magnitude.

Measurements on pure P(VDF–TrFE) capacitors with a Sawyer–Tower circuit showed a coercive field of $50\,MV\,m^{-1}$ and a remanent polarization of $60\,mC\,m^{-2}$, in good agreement with literature data[13]. The polarization cannot be determined for the P3HT:P(VDF–TrFE) mixtures, because the presence of the conducting P3HT phase causes too high leakage currents. To demonstrate that the ferroelectric properties are maintained in the mixtures, the dielectric constant was determined from capacitance–voltage (C–V) measurements and plotted as a function of applied electric field in Fig. 2b. The maxima, which occur at fields slightly different from the coercive field, and the hysteresis both stem from the irreversible ferroelectric polarization, that is, dipole rotation in the presence of an electric field that leads to a typical butterfly shape[14], which is retained on blending P3HT into the ferroelectric (Fig. 2b).

Switching is demonstrated in Fig. 3a for a ferroelectric junction with 10 wt% P3HT sandwiched between two silver contacts. The current density for the pristine, unpoled junction is low, showing that silver is a poorly injecting contact. Subsequently, the junction is poled at −20 V with respect to the bottom electrode. As explained in Fig. 1, the charge injection at the bottom electrode is improved, whereas that of the top electrode remains poor. At positive bias, charges are injected from the bottom contact and the current

© 2008 Macmillan Publishers Limited. All rights reserved.

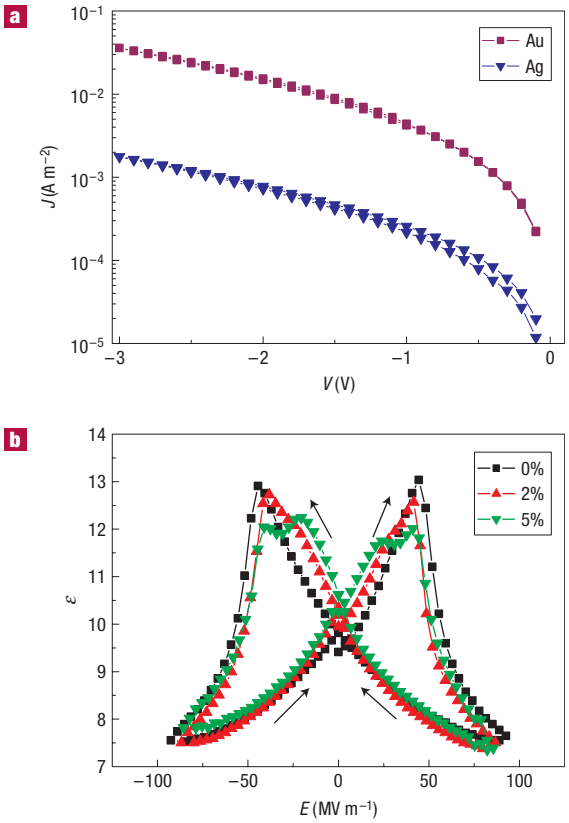

Figure 2 Electrical transport of a pristine, unpoled, polymeric semiconductor–ferroelectric interpenetrating network. a, *J–V* characteristics of a diode with 5% P3HT mixed in the ferroelectric matrix of P(VDF–TrFE) with either two Au or two Ag electrodes. **b**, Dielectric constant as determined from capacitance–voltage measurements of devices with different blending ratios.

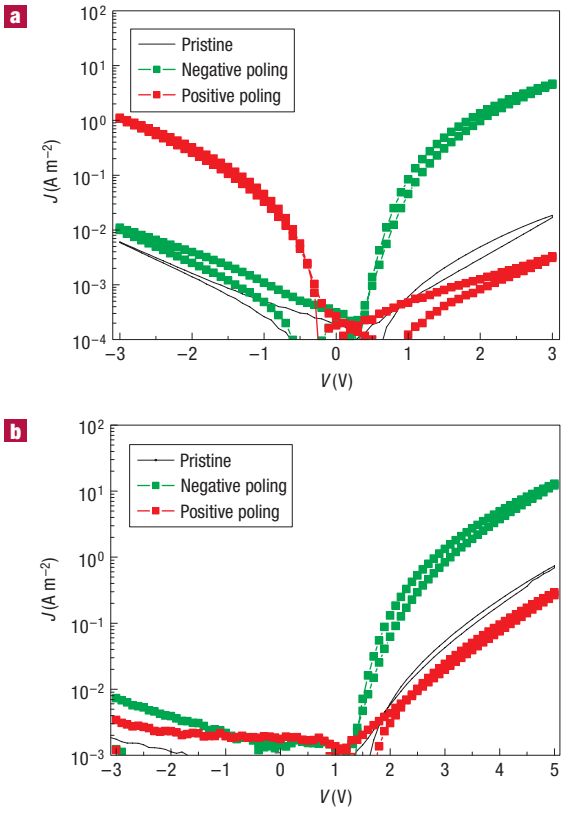

Figure 3 Resistance switching by ferroelectric polarization. a, *J–V* characteristics of a diode based on a network of P(VDF–TrFE):P3HT (10:1) with two Ag contacts for the pristine film, and after positive and negative polarization. **b**, *J–V* characteristics of a diode consisting of P(VDF–TrFE):P3HT (10:1) with Ag bottom electrode and blocking LiF/Al top electrode for the pristine film, and after positive and negative polarization.

density is about two orders of magnitude larger than that of the unpoled junction. At reverse bias, charges have to be injected from the top contact into the depleted semiconductor. Thus injection is poor and no change in current density is observed: the poled junction is a rectifying diode. When the device is poled with opposite polarity, at +20 V, the charge injection at the top electrode is improved whereas that of the bottom electrode becomes poor. The poled junction is again a rectifying diode, but in the reverse direction. The junction is bistable and can be switched between two rectifying states with opposite polarities.

The switching mechanism as proposed in Fig. 1d relies on a semiconducting phase being continuous between the electrodes. We note that the devices with Ag top and bottom electrodes are electrically symmetric, demonstrating that the electrode–blend interfaces are identical. Hence, the phase separation as observed by atomic force microscopy and scanning near-field optical microscopy is contained throughout the film. To further elucidate the switching mechanism we also added a 60-nm-thick semiconducting polymer film between the blend and the Ag contact. As expected, no switching occurred, because the accumulated charges due to the poling of the ferroelectric are too far away from the metal–semiconducting interface to modify the charge injection.

The most economic solid-state memory is a cross-point array with a non-patterned storage medium[15]. The storage medium is sandwiched between two layers of electrodes running in perpendicular directions. These rows and columns form the word and bit lines. However, a major bottleneck for a memory array based on resistive elements is that additional diodes have to be incorporated to prevent cross-talk between the cells. We demonstrate that an integrated switch and diode can be achieved by using a blocking contact with a low work function. The electrical transport for a ferroelectric junction with 10 wt% P3HT sandwiched between a Ag bottom contact and a LiF/Al blocking top contact is presented in Fig. 3b. The forward current density of the pristine, unpoled junction is limited by the poorly injecting Ag bottom contact, whereas the reverse current is blocked by the LiF/Al contact. When we pole the junction at −20 V the bottom Ag contact becomes a good injecting contact and the forward current density increases. When we pole the junction at +20 V the poor injection properties of the bottom Ag contact deteriorate even further and the forward current density decreases. The junction is now a rectifying bistable resistive switch[16].

Measurements of degradation and programming time, which are the critical parameters to compare with competing technologies, are shown in Fig. 4 for a typical ferroelectric device with 10 wt% P3HT. Pulse measurements were made to determine the switching time. Figure 4a shows that switching is symmetric and is about 0.5 ms. The retention was measured over 11 days. Figure 4b shows that there is no change in current modulation.

© 2008 Macmillan Publishers Limited. All rights reserved.

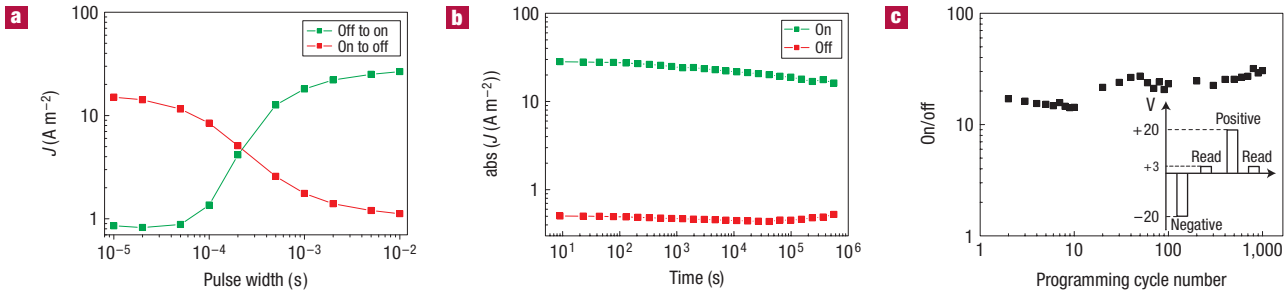

Figure 4 Programming properties of ferroelectric memories consisting of a P(VDF–TrFE):P3HT (10:1) network sandwiched between two Ag electrodes. a, The programming time measurement for the ferroelectric device made by bringing the device to the on state and trying to switch to an off state and vice versa with a ±20 V pulse with varying pulse widths and monitoring the current at +3 V after application of each pulse. **b**, Data retention time obtained by programming the device once to on or off state and monitoring the current over time at +3 V. **c**, Programming cycle endurance obtained as the ratio of the on- and off-state electrical currents measured at +3 V as a function of the number of programming cycles (negative–read–positive–read), as depicted in the inset.

The long retention time is typical for ferroelectric capacitors[4] and field-effect transistors[17]. The cycle endurance is presented in Fig. 4c. The ratio between on and off current on repeated switching remains constant, as shown in Fig. 4c, so there is no deterioration of the current modulation on cycling. The long retention time and high programming-cycle endurance strengthen the viability of this device architecture for non-volatile memory applications.

In summary, we have demonstrated a general concept to integrate mutually exclusive electronic properties into a single material by blending of two electronic components into a phase-separated interpenetrating network. Non-volatile bistable diodes are realized that are based on an interpenetrating network of a polymeric ferroelectric and a polymeric semiconductor. In such a diode poling of the ferroelectric phase modifies the charge injection of the electrode into the semiconducting phase. Junctions with two poorly injecting contacts can switch between two rectifying states with inverse polarity. Junctions with one blocking contact (LiF/Al) and one poorly injecting contact (Ag) form a rectifying bistable resistive switch that can be read out non-destructively.

METHODS

The ferroelectric polymer (P(VDF–TrFE)) was purchased from Solvay. Regio-irregular (regio-random) P3HT (rir-P3HT, purchased from Rieke Metals) was chosen because of ease of processing and better solubility. Rir-P3HT was purified by dissolving in distilled toluene, dedoping with hydrazine and precipitating in methanol. The fraction collected was Soxhlet extracted with methanol, *n*-hexane and CH_2Cl_2 until the extraction solvent was colourless. The dichloromethane fraction was precipitated in methanol, collected, dissolved in chloroform and precipitated again in methanol. The collected fraction is dried under vacuum and stored in the glove box under N_2 atmosphere.

Fabrication of an interpenetrating network requires a common solvent for both P(VDF–TrFE) and the polymeric semiconductor rir-P3HT. The solutions for processing were prepared by dissolving 30–50 mg ml^{-1} of P(VDF–TrFE) (65-35) in THF for a pure ferroelectric layer. The 1:100 P3HT:P(VDF–TrFE) (1% P3HT) blend was prepared by adding 1 mg P3HT to 100 mg P(VDF–TrFE) dissolved in THF. Similarly the following ratios could be prepared: 1:50 (2% P3HT), 1:40 (2.5% P3HT), 1:30 (3.3% P3HT), 1:20 (5% P3HT) and 1:10 (10% P3HT).

As bottom electrode, Ag or Au is evaporated on cleaned glass substrate with a 1 nm Cr adhesion layer. The solution is spin coated on the substrate in a nitrogen-filled glove box after filtration with 1 μm PTFE filters. The stack is annealed in a vacuum oven for 2 h at 140 °C to enhance the crystallinity of the P(VDF–TrFE) phase. Electrodes were evaporated on top of the film through a shadow mask. The dimension of the active area is varied from 4 mm × 4 mm to 0.3 mm × 0.3 mm. All devices were characterized in vacuum (~10^{-6} mbar) and dark. Current–voltage measurements were carried out with a Keithley 2400 and capacitance–voltage measurements were made with an Agilent 4284A. To switch the devices, pulses of ±20 V were applied to the device from an Agilent 8114A pulse generator. Hundreds of devices were tested, and all showed identical switching behaviour. Fluctuations of the current density in the on state remain within 5%, whereas the low current in the off state is in some cases dominated by the device leakage current. Then the higher leakage current results in lower on/off-state current ratios. The ferroelectric (P(VDF–TrFE)) (65–35) was sandwiched between two silver electrodes and characterized using a Sawyer–Tower circuit, giving a coercive field of 50 MV m^{-1} and a remnant polarization of 60 mC m^{-2}.

Received 4 December 2007; accepted 14 May 2008; published 15 June 2008.

References

1. Scott, J. C. & Bozano, L. D. Nonvolatile memory elements based on organic materials. *Adv. Mater.* **19**, 1451–1463 (2007).
2. Scott, J. F. & Paz de Araujo, C. A. Ferroelectric memories. *Science* **246**, 1400–1405 (1989).
3. Scott, J. F. *Ferroelectric Memories* (Springer, Heidelberg, 2000).
4. Dawber, M., Rabe, K. M. & Scott, J. F. Physics of thin-film ferroelectric oxides. *Rev. Mod. Phys* **77**, 1083–1130 (2005).
5. Blom, P. W. M., Wolf, R. M., Cillessen, J. F. M. & Krijn, M. P. C. M. Ferroelectric Schottky diode. *Phys. Rev. Lett.* **73**, 2107–2110 (1994).
6. Halls, J. J. M. *et al.* Efficient photodiodes from interpenetrating polymer networks. *Nature* **376**, 498–500 (1995).
7. Yu, G., Gao, J., Hummelen, J. C., Wudl, F. & Heeger, A. J. Polymer photovoltaic cells: Enhanced efficiencies via a network of internal donor–acceptor heterojunctions. *Science* **270**, 1789–1791 (1995).
8. Pei, Q., Yu, G., Zhang, C., Yang, Y. & Heeger, A. J. Polymer light-emitting electrochemical cells. *Science* **269**, 1086–1088 (1995).
9. Meijer, E. J. *et al.* Solution-processed ambipolar organic field-effect transistors and inverters. *Nature Mater.* **2**, 678–682 (2003).
10. Chua, L. L. *et al.* General observation of n-type field-effect behaviour in organic semiconductors. *Nature* **434**, 194–199 (2005).
11. Kodama, H., Takahashi, Y. & Furukawa, T. Effects of annealing on the structure and switching characteristics of VDF/TrFE copolymers. *Ferroelectrics* **203**, 433–455 (1997).
12. Van Duren, J. K. J. *et al.* Injection-limited current in a methanofullerene. *J. Appl. Phys.* **94**, 4477–4479 (2003).
13. Lovinger, A. J. Ferroelectric polymers. *Science* **220**, 1115–1121 (1983).
14. Takahashi, T., Date, M. & Fukada, E. Dielectric hysteresis and rotation of dipoles in polyvinylidene fluoride. *Appl. Phys. Lett.* **37**, 791–793 (1980).
15. Scott, J. C. Is there an immortal memory? *Science* **304**, 62–63 (2004).
16. Asadi, K., Blom, P. W. M. & de Boer, B. Patent Appl. Nr. EP 07108645.8-2203 (2007).
17. Naber, R. C. G. *et al.* High performance solution-processed polymer ferroelectric field effect transistors. *Nature Mater.* **4**, 243–248 (2005).

Supplementary Information accompanies this paper on www.nature.com/naturematerials.

Acknowledgements

The authors acknowledge the contributions of R. C. G. Naber and D. M. Jarzab to this work, J. Harkema for technical assistance, R. Coehoorn and E. Meulenkamp for stimulating discussions and both the Zernike Institute for Advanced Materials and the EC project PolyApply IST-IP-507143 for financial support.

Author information

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions.
Correspondence and requests for materials should be addressed to P.W.M.B.

© 2008 Macmillan Publishers Limited. All rights reserved.